Title: **"A PROCESS FOR MANUFACTURING A PTFE FILAMENT, AND A PTFE FILAMENT OBTAINED BY THIS PROCESS".**

This invention refers to a process of manufacturing a polytetrafluoroethylene (hereinafter called "PTFE") filament, and the filament obtained by this process.

Since the development of the material in the United States Patent No. 3,953,566 by Gore, flexible fibers made from expanded PTFE have been used for several purposes, such as fabric, sewing thread and dental floss. Such fibers are widely used due to the very good physical properties of the PTFE resin, and, furthermore, as they are chemically inert, have excellent high and low temperature performance, high resistance to ultraviolet radiation and are highly lubricious. United States Patents 3,953,566 and 3,962,153 disclose processes for producing highly porous materials from PTFE that result in very high strength products. These patents disclose how strands made of this polymer are produced by paste forming techniques, where the polymer is converted into a paste and shaped into a strand, which is then expanded by stretching in one or more directions under certain conditions so that it becomes much more porous and stronger. This phenomenon of expansion accompanied by an increase in strength occurs with certain preferred PTFE resins and within preferred ranges of stretching rate and preferred temperature ranges. Accordingly, most of the products are obtained when expansion is carried out at high temperatures, preferably within the range of 35° C to 327° C.

In addition, it was found that some resins are much more suitable for the expansion process than others, since they can be processed over a wider range of stretching rate and temperature. The primary requisite of a suitable resin is a very high degree of crystallinity, preferably in the range of 98% or above.

The porous microstructure of the expanded material is affected by the temperature and the rate at which it is expanded. The structure consists of nodes interconnected by very small fibrils. In the case of uni-axial expansion the nodes are elongated, the longer axis of a node being oriented

perpendicular to the direction of expansion. The fibrils that interconnect the nodes are oriented parallel to the direction of expansion. The nodes may vary in size, depending on the conditions used in the expansion. Products which have been expanded at high temperatures and high rates have a more homogeneous structure, i.e., they have smaller and more closely spaced nodes, and these nodes are interconnected with a greater number of fibrils. These products are also found to have much greater strength. The expansion process results in a tremendous increase in the tensile strength of the PTFE fibers and an increase in the porosity.

When the expanded products are heated to a temperature above the lowest crystalline melting point of the PTFE, disorder begins to occur in the geometric order of the crystallites and the crystallinity decreases, therefore increasing the amorphous content of the polymer, typically to 10% or more. These amorphous regions within the crystalline structure appear to greatly inhibit slippage along the crystalline axis of the crystallite and appear to lock fibrils and crystallites so that they resist slippage under stress. Therefore, the heat treatment may be considered an amorphous locking process. The important aspect of amorphous locking is that an increase in amorphous content occurs, regardless of the crystallinity of the resin at start. When the material is heated above 327° C a surprising increase in strengths occurs.

The increase in strength of the polymer matrix is dependent upon the strength of the extruded material before expansion, the degree of crystallinity of the polymer, the rate and temperature at which the expansion is performed, and amorphous locking. When all these factors are employed to maximize the strength of the material, tensile strengths of 10,000 psi and above, with porosity of 90% or more are obtained. In contrast, the maximum tensile strength of conventional extruded or molded PTFE after sintering is generally considered to be about 3,000 psi, and for conventional extruded and calendered PTFE tape, which has been centered, the maximum is about 5,100 psi.

The prior art in dental floss, as exemplified by the U.S. Patents Nos. 3,830,246, 3,897,795, 4,215,478 and 4,033,365, is made of synthetic or

natural material. PTFE is not mentioned.

These patents show that flossing is an extremely important adjunct to proper dental hygiene. The insufficient consumer acceptance, despite often repeat directions by dentists to use floss, may arise from the fact that prior art flosses frequently caused gingival bleeding and are generally uncomfortable or difficult to use. Those conditions may arise primarily from the relatively high coefficient of friction (COF) of such flosses.

Thus, because prior art flosses have such high coefficients of friction, consumers must use substantial force to pull them between the teeth or so-called "contact points". Unfortunately, the user does not know when the floss will, in fact, pass between the contact points. When this suddenly occurs, the user does not have time to release the great force being applied. This appears to cause the flosses to be pulled into the gum, causing cuts that bleed, sometimes profusely. Hence, many of the dental flosses presently on the market have received limited consumer acceptance. The lack of consumer acceptance of any single dental floss on the market is due, in part, to the propensity of dental floss to cause gingival bleeding. In addition, dental floss is generally considered difficult and uncomfortable to use. The consumer dissatisfaction with some dental flosses is caused by the relatively high coefficient of friction.

In order to solve this problem a new type of dental floss made from PTFE has become available from a variety of sources. This type of dental floss has certain beneficial characteristics, including high lubricity and a lower fraying rate than conventional flosses. Some patents have been aimed at such products including U.S. Patents Nos. 5,033,488 and 5,209,251 to Curtis et al., and U.S. Patent No. 5,220,932 to Blass.

The Curtis patents (U.S. Patents Nos. 5,033,488 and 5,209,251) disclose the use of high strength expanded PTFE, which is coated with a material to increase the PTFE coefficient of friction for use as a dental floss.

The Blass patent (U.S. Patent No. 5,220,932) discloses the use of a uni-axially stretched, non-porous PTFE having a relatively low tensile strength, and is coated with wax to increase the PTFE coefficient of friction

for use as a dental floss.

Expanded PTFE has a rather low coefficient of friction (below 0.08) compared to a coefficient of friction of about 0.2 for prior art commercial flosses. The inventors in U.S. Patent No. 5,033,488 show that microcrystalline wax (MCW) adheres to expanded PTFE and, unexpectedly, provides a coefficient of friction sufficiently high to permit the user to securely grasp the floss and tapes, but generally not so high as that of the prior art. This coefficient of friction is intermediate between the very low coefficient of friction of expanded PTFE (below 0.08) and coefficient of friction of commercial flosses, say about 0.08 and 0.15.

Other patents, such as U.S. Patents Nos. 5,657,779 and 5,806,539 teach a method for producing PTFE dental floss, comprising the passage of an unsintered PTFE tape across a heated surface in sliding contact therewith, while applying tension to the tape, wherein the temperature of the heated surface, the passage speed of the tape and the tension applied are such that the PTFE tape, when its temperature is raised by contact with the heated surface, is longitudinally stretched. The dental floss produced comprises a PTFE tape having opposite faces at which the respective physical states of the PTFE material differ, the coefficient of friction being one of these differences. The opposite faces of this dental floss have different degrees of sintering.

The U.S. Patent No. 5,698,300 to Lenzing discloses a film consisting of two or more PTFE layers which differ in their shrink properties providing a bi-component fiber, which can be transformed into a staple crimp by heating to a temperature above 200° C. This U.S. patent further relates to a process for producing a bi-component film from two types of PTFE. The resultant film shrinks to different extents under the effect of heat and differs in its hot-air shrinkage by at least 1 %. Each type of PTFE is molded in a cylinder and one half is joined to the other half with the other type of PTFE and then extruded, calendered, dried, sintered and cut into a staple fiber.

The U.S. Patent No. 5,804,290 by Lenzing describes a dental floss that contains PTFE and whiting filler, and preserves the gum more than

the prior art. By adjusting the amount of whiting material, the kinetic friction of the dental floss can be modified. Experiments have disclosed that dental floss containing whiting from 0.1 to 15% by weight is particularly well suited.

The U.S. Patent No. 6,220,256 also discloses a dental floss made of PTFE and filler, this filler being fumed silica. The dental floss can have a plurality of layers of PTFE , with at least one of the layers having fumed silica placed within it. Preferably, the filament has an inner layer and two outer layers, with the fumed silica situated in at least one of the two outer layers. The layers are made separately and then laminated by any conventional lamination technique, such as calendering together with use of rotating rollers. The floss obtained through this document provides increased surface friction.

In view of the above, it is an objective of the present invention to provide a bi-color bi-component expanded PTFE dental floss where each side presents different coefficients of friction.

Another objective of the present invention relies on providing a dental floss that permits the consumers to choose the side that they intend to use.

Another objective of the present invention relies on providing a dental floss with sides of different colors to aid identification of the side that is more or less slippery.

Another objective of the present invention relies on providing a filament with sides having different coefficients of friction for other applications besides dental floss.

Accordingly, an inventive process for manufacturing a PTFE filament of the type comprising steps of extrusion, and, subsequently, stretching, heating and cutting, and an inventive PTFE filament obtained by this process, are provided.

The process of the present invention comprises the following steps prior to extrusion:

providing a recipient, which preferably consists of a cylinder of a pre-form machine, having rigid side walls;

arranging a first mixture containing PTFE and a filler, and a second mixture containing PTFE, inside the recipient, side by side and aligned with the side walls; and

pressing the first and second mixtures in a direction parallel to the side walls to form a billet in which the first and second mixtures have different coefficients of friction.

After these steps, the billet having the first and second mixtures is extruded to form a strand, which is subsequently stretched, heated, rolled and cut by known processes in the art to form the inventive PTFE filament.

The filler has the purpose of providing a different coefficient of friction on each side of the PTFE filament. Accordingly, the coefficient of friction on the side with filler preferably ranging from 0.08 to 0.20, and the side without filler being less than 0.08. The filler can be made of silica, alumina, mica and/or calcium carbonate, among other components.

Although, in a preferred embodiment, the second mixture does not contain such a filler, other embodiments of the present invention can present a first mixture with a first filler and a second mixture with a second filler, provided that the billet formed includes first and second mixtures having different coefficients of friction.

In addition, unlike prior arts, the first and second mixtures may also have the same shrink properties, as the above difference in the coefficient of friction between the mixtures is provided by the filler.

In an embodiment of the present process, different pigments made of organic and inorganic materials may be mixed with the mixtures so that each mixture can have a different color.

In the above or any other embodiment of the present invention, the step of arranging can also comprise a step of inserting a barrier, preferably a plate, in the recipient to separate it into two portions. Although, in a preferred embodiment, this barrier is a plate, other embodiments for the barrier can be used without affecting the scope of the present invention. Then, the first and the second mixtures are respectively inserted into these two portions of the recipient. Subsequently, this barrier is removed, enabling a part

of the first mixture to contact a part of the second mixture and be arranged by side by side and aligned with the side walls of the recipient.

The PTFE filament obtained comprises one side with a filler and another side without filler, so that these sides have different coefficients of friction, wherein preferably the side with filler presents a higher coefficient of friction than the other side. Also, in a preferred embodiment, the filament presents each side with a different color.

Brief description of the drawings

Fig. 1 is a perspective view of a plate being inserted into a cylinder of a pre-form machine according to the preferred embodiment of the present invention.

Fig. 2 is a perspective view of the cylinder including the plate according to the embodiment depicted in figure 1.

Fig. 3 is a perspective view of the cylinder including the plate and mixtures A and B according to the embodiment depicted in figure 1.

Fig. 4 is a perspective view of the plate being removed from the cylinder according to the embodiment depicted in figure 1.

Fig. 5 is a perspective view of a billet formed after the mixtures A and B are pressed in the cylinder according to the embodiment depicted in figure 1.

Fig. 6 is a perspective view of a strand formed after the billet is extruded according to the embodiment depicted in figure 1.

Fig. 7 is a perspective view of a PTFE filament according to the embodiment depicted in figure 1.

Detailed Description

The invention will now be described in further detail on the basis of tests and examples.

Steps in the process:

(a) Mixture / Paste-Extrusion / Tape

Two mixtures, A and B, are produced in the following manner:

A – A fine-powder PTFE resin is pre-mixed with silica or alumina filler and then a liquid lubricant is added until a compound is formed.

B – A fine-powder PTFE resin is mixed with a liquid lubricant, until a compound is formed.

The first and the second mixtures preferentially have the same shrink properties, and, furthermore, in one or both mixtures a pigment is added for identification of the compositions.

The volume of lubricant used in these mixtures should be sufficient to lubricate the primary particles of the PTFE resin so as to minimize the possibility of shearing of the particles prior to extruding. The proportion ranges from 17% to 29%. In mixtures, the amount of filler can vary from 0% to 25 % and the amount of pigment ranges from 0% to 10%. These mixtures are processed, preferably for 20 to 30 minutes.

Other kinds of filler besides silica and alumina can be used in the compound and the pigments can be organic or inorganic.

As indicated in figures 1 to 5, a cylinder of a pre-form machine 1 is previously axially split along its length into two halves by a plate 2 or strip and then the mixture A is fed into one half and the mixture B into the other half. After feeding the cylinder 1 with the different compounds, the plate 2 that separates the same into equal parts is taken out and the material is preformed. Consequently, a bi-color bi-component billet 5 is formed, wherein one half comprises mixture A and the other comprises mixture B, and, furthermore, presenting excellent adhesion at the interface of the mixtures.

After these steps, the billet 5 having the mixtures A and B is extruded to form a strand 6, as depicted in figure 6, which is subsequently rolled, stretched, heated and cut by known processes in the art to form the inventive PTFE filament (figure 7), as follows.

In the extrusion process, a reduction ratio of about 10:1 to 1000:1 may be used (i.e. reduction ratio = cross-sectional area of extrusion cylinder divided by cross-sectional area of the extrusion die). For most applications, a reduction ratio of 25:1 to 200:1 is preferred.

The strand is, in the next stage, pressed through calender rolls in order to form a tape with a thickness ranging from 50 μm to 1000 μm. In this method, care should be taken that the strand runs in between the rollers

such that the imaginary separating line of the two material halves lies parallel to the roller nip. Then a bi-color bi-component tape is produced, where one side consists of PTFE-filler and the other side is composed of pure PTFE. These sides can be of a variety of colors. The tape resulting from the calendering, with one side one color and the other side another color, passes through a drying oven to remove the liquid lubricant. The drying temperature ranges from 100°C to 300°C.

(b) Stretching and heat treatment

In this invention, it has been found that such composite tape can be expanded by stretching in at least one direction about 1.1 to 100 times its original length (with about 2 to 50 times being preferred). The stretching is carried out by passing the dry composite tape through tensioning rollers between the two units of pulling rollers that operate with a stretching ratio – that is, the ratio between the entry speed and the exit speed – from 1.1 to 100, and a stretching temperature ranging from 150 to 300°C. The expanded PTFE composite tape can be optionally longitudinally expanded further if desired. The heat element in the expansion process may be an oven, a hot-air, steam or high-boiling-point liquid heater, a heated plate or a heated cylinder.

After the stretching, the composite tape is wound in a winder.

The tape may be formed into filaments by slitting the expanded composite tape into pre-determined widths (between 0.5 to 10 mm), feeding it into the cutting unit, whereby the individual PTFE filaments are cut and separated.

Following cutting, the composite expanded PTFE filaments, where one side is composed of PTFE-filler (one color) and the other side of pure PTFE (another color), may then be further stretched. The composite filament is again stretched with a stretching ratio ranging from 1.1 to 20 (with 1.2 to 8.0 being preferred) under high temperature (between 300 to 450°C) in order to subject the fiber to an amorphous locking step. The stretched filaments are wound individually in the winding unit.

The expanded PTFE filament obtained from the technique described above is depicted in figure 7, reference number 7, and presents two

sides with different characteristics, principally their coefficients of friction, determined according to the method described below. On side A, the filament contains PTFE-filler (one color) and, on side B, contains pure PTFE (another color).

The final characteristics of the dental floss comprise: a width of about 0.5 to 3.0 mm; a thickness of about 20 to 400 μm; a weight/length of about 400 to 2000 dtex; a density of about 0.7 to 2.2 g/cm^3; a tensile strength ranging from 100 to 1100 MPa and a tenacity ranging from 2.0 to 6.0 cN/dtex. The coefficient of friction on both sides are different, the side with filler ranging from 0.08 to 0.20 and the side without filler being less than 0.08.

Each of these properties is measured in the following manner: length, width and thickness are determined through the use of calipers; density by dividing the measured weight of the sample by the computed volume of the sample; the volume is computed by multiplying the measured length, width and thickness of the sample.

The bulk tensile strength of the fibers is measured by a tensile tester, such as an INSTRON Machine by using the following conditions: The gauge length is 250 mm and the cross-head speed of the tensile tester is 250 mm/min.

Tenacity is calculated by dividing the maximum force obtained in the tensile tester by its normalized weight per unit length (tex (grams/1,000 meters) or dtex (grams/10,000 meters) or denier (grams/9,000 meters)).

The coefficient of friction is a dimensionless quality which represents the force required to move an object across a surface. This test method covers the measurement of kinetic friction between fiber and solid surfaces of a constant radius in the contact area. In general, the greater the value of the coefficient of friction, the more difficult it is to move the object with respect to the surface, and thus, a greater frictional force is involved. Various properties of dental floss can be inferred from coefficient of friction experiments, such as ease of inter-proximal access and gentleness of the floss on gingival tissue.

Apparatus required for determination of the coefficient of friction:

Instron Machine, friction testing apparatus – with rotating mandrels and 100g weight.

Procedure:

Preset the Instron with the following parameters:

Cross-head weight – 5 Kg

Cross-head speed – 190 mm/min

Gauge length – 110 mm

Reference weight – 100 g

Angle of wrap – 240 = 4.189 rad

Recorder speed – 5 cm/min

(1) Measure 5 pieces of floss, each110 mm in length

(2) Attach one strand of floss to upper cross-head. Let it hang between the mandrels, not touching them.

(3) Place a 100 g weight at the other end of the sample.

(4) Measure the force recorded by the recorder resulting from the weight and the floss sample. When the floss and weight are raised by the Instron unit, this value remains constant. This value is the resting weight.

(5) To measure the coefficient of friction, wrap the floss sample around two mandrels

(6) Make sure that the floss is not twisted and is very steady

(7) Zero the chart recorder and start

(8) Start the mandrels rotating

(9) Press the start button to start raising the floss over the rotating mandrels

(10) Let the Instron raise the floss to approximately 3 inches from the 100 g weight

(11) Select 10 peaks from chart recorder and average this data

(12) Perform calculation below on average this data:

coefficient of friction = (1/0) * ln (T2/T1)

Where:

coefficient of friction = coefficient of friction

0 = angle of wrap in radius

T2 = tension while system is being pulled over mandrels

T1 = tension in floss sample + weight at rest

(13) Repeat steps 5 –12, four more times, using a new floss sample every time.

A few examples will be described hereinafter on the basis of tests performed under different conditions:

Example 1:

A bi-color bi-component dental floss of the present invention is produced as described below:

Two mixtures, A and B, are produced in the following manner:

A – A fine-powder PTFE resin is pre-mixed with quartz silica filler and then a liquid lubricant is added until a compound is formed.

B – A fine-powder PTFE resin is pre-mixed with an organic pigment and then a liquid lubricant is also added until a compound is formed.

These mixtures are processed preferably for 20 to 30 minutes and should have the same pressure extrusion. The proportion of lubricant in these mixtures ranges from 17% to 29%. In mixture A, the amount of quartz silica is 4.7% and in the mixture B the amount of pigment is 0.5%.

The cylinder of a pre-form machine 1 is fed with the mixture A in one half and the mixture B in another half (figure 3). After feeding the cylinder 1 with the different compounds, the plate 2 that separates the same into equal parts is removed and the material is pre-formed (figure 4). Consequently, a bi-color bi-component billet 5 is formed, wherein one half comprises mixture A and the other comprises mixture B (figure 5).

After these steps, this billet is extruded to form a strand 6 (figure 6), which is subsequently rolled, stretched, heated and cut by known processes in the art to form the inventive PTFE filament, as follows.

A reduction ratio of 148:1 is used. The bi-color bi-component tape resulting from calender rolling, one side of which is white (PTFE-quartz silica) and the other colored side (PTFE-pigment), with a thickness of 400 μm. This tape is passed through an oven at a temperature of 220°C for lubricant removal. The dry tape is stretched uni-axially in the longitudinal direction

8.0 times its original length by passing the dry tape through tensioning rollers between the two units of pulling rollers that operate with a stretching ratio of 8.0 and a stretching temperature of 265°C.

The expanded tape is slit to 3.0 mm widths by passing it between a set of gapped blades. The slit strands are further stretched uniaxially in the longitudinal direction over hot plates at a temperature of 400°C and at a ratio of 4.0 to form a bi-color bi-component dental floss.

The following measures are taken on the bi-color bi-component expanded PTFE dental floss:

Filament Number:	850 dtex
Tensile Strength:	420 MPa
Tenacity:	3.3 g/dtex
Coefficient of friction: White side	0.08
Colored side	0.06

Example 2:

A bi-component dental floss is produced, as described in Example 1. The difference is in the composition of the mixtures. The proportion of quartz silica in the white side is 12.3%.

The following measures are taken on the bi-color bi-component expanded PTFE dental floss:

Filament Number:	870 dtex
Tensile Strength:	340 MPa
Tenacity:	2.8 g/dtex
Coefficient of friction: White side	0.10
Colored side	0.06

Example 3:

A bi-component dental floss is also produced, as described in Example 1. In this case, the type of filler used is precipitated silica (white side) in the proportion of 8.2%.

The following measures are taken on the bi-color bi-component expanded PTFE dental floss:

Filament Number:	860 dtex

Tensile Strength:	400 MPa
Tenacity:	3.1 g/dtex
Coefficient of friction: White side	0.10
Colored side	0.06

Example 4:

A bi-component dental floss is also produced, as described in Example 1. Alumina is the filler, used in the proportion 12%.

The following measures are taken on the bi-color bi-component expanded PTFE dental floss:

Filament Number:	870 dtex
Tensile Strength:	350 MPa
Tenacity:	2.8 g/dtex
Coefficient of friction: White side	0.09
Colored side	0.06

Although described in connection with specific examples, the present invention is not intended to be limited thereto, but rather includes such modifications and variations as are within the scope of the appended claims.